LAPW vs. LMTO full-potential simulations and anharmonic dynamics of $KNbO_3$

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Abstract. With the aim to get an insight in the origin of differences in the earlier reported calculation results for $KNbO_3$ and to test the recently proposed "NFP" implementation of the full-potential linear muffin-tin orbital (FP-LMTO) method by M. Methfessel and M. van Schilfgaarde, we perform a comparative study of the ferroelectric instability in $KNbO_3$ by FP-LMTO and full-potential linear augmented plane-wave (LAPW) method. It is shown that a high precision in the description of the charge density variations over the interstitial region in perovskite materials is essential; the technical limitations of the accuracy of charge-density description apparently accounted for previously reported slight disagreement with the LAPW results. With more accurate description of the charge density by sufficiently fine real-space grid, the results obtained by both methods became almost identical.

In order to extract additional information (beyond the harmonic approximation) from the total energy fit obtainable in total-energy calculations, a scheme is proposed to solve the multidimensional vibrational Schrödinger equation in the model of non-interacting anharmonic oscillators via the expansion in hyperspherical harmonics. Preliminary results are given for the t_{1u} vibrational modes in cubic $KNbO_3$.

INTRODUCTION

$KNbO_3$ is one of benchmark systems for *ab initio* analysis of ferroelectric perovskites. It has been extensively studied by the whole spectrum of numerical methods from an apparently ultimately accurate full-potential linear augmented plane waves (LAPW) [1–5] through pseudopotentials [6] and tight-binding *ab initio* schemes [7] to semiempirical and model-based techniques [8].

Modern state-of-art simulations of ferroelectric correlations, lattice dynamics and phase transitions are dependent on reliable and accurate description of the total energy as function of displacements and strain variables. The full-potential linear muffin-tin-orbitals (FP-LMTO) method [9] was proven able to provide a reasonable balance of accuracy and low computational effort even when applied to supercells of up to 40 atoms [10–13]. However, in sensitive benchmark calculations of Γ phonons,

due to certain technical limitations, FP-LMTO provided apparently lower accuracy for phonon eigenvectors, as compared to FP-LAPW [11,3,5]. A new version of the FP-LMTO code by Methfessel and van Schilfgaarde [14], in contrast to the previous one used in our earlier calculations [9], is unsensitive to sphere packing and uses much more efficient, albeit more mathematically involved, basis of augmented "smooth Hankel functions" that enables one to drastically reduce the size of diagonalization problem without loss of accuracy. We compare the results obtained with the new FP-LMTO and with the WIEN97 implementation of the FP-LAPW method [15], concentrating on the accuracy and performance.

In order to get an additional insight into lattice dynamics of $KNbO_3$, we present vibrational frequencies as calculated quantum-mechanically in the assumption of uncoupled multidimensional anharmonic oscillators, based on the total energy data obtained from first-principles calculations, and give a preliminary estimate of the lowest vibration frequency within this approach.

COMPARISON OF CALCULATION METHODS

The linear augmented plane-wave (LAPW) and the linear muffin-tin orbital (LMTO) methods are closely related and originate in the same work by Andersen [16]. In the modern stage at their development, they share the advantage of being all-electron methods (in contrast to pseudopotential ones and to those depending on the frozen-core approximation). As compared to tight-binding schemes with fixed (e.g. Gaussian-type) bases, the basis in LAPW and LMTO is optimized in the course of iterations, as the heads of wavefunctions are recalculated inside the (arbitrarily) chosen muffin-tin spheres from one iteration to another. The tails of basis functions that span the interstitial region between the spheres are constructed by an augmentation procedure which matches the numerical solutions inside the MT-spheres either to the plane waves of different $\mathbf{k}$ (in LAPW) or to the spherical Hankel functions of different energy (in LMTO). This difference accounts for relative advantages and disadvantages of these two calculation schemes. In LAPW, the number of augmented plane waves with different $\mathbf{k}$ can be safely saturated, until the desirable convergence of results with respect to the completeness of basis is achieved. This however has its price in terms of computational effort.

The advantage of LMTO lies in the fact that its basis functions may be tuned to resemble true atom-centered wavefunctions in a crystal. This means, in the ideal case, quite efficient and compact basis set and hence computational speed and the ability to treat larger systems than is possible with LAPW, given certain amount of computer resources. The weak point of LMTO is that the saturation of the basis set is not as straightforward as in the LAPW, because adding more atom-centered tail functions of certain angular symmetry needs care to prevent linear dependences within the basis set. In order to overcome this problem and at the same time to maintain the LMTO as, ideally, the 'minimal basis' method of competitive accuracy, one can try to experiment with more sophisticated but hopefully more efficient

envelope functions. As some examples of proposed alternatives to conventional spherical Hankel functions one can single out the tight-binding LMTO method [17] or the "exact muffin-tin orbital theory" development [18], both of them being not yet implemented, to our knowledge, in workable full-potential total-energy codes.

Recently, yet another extension within the general LMTO formalism has been proposed and implemented by M. Methfessel and M. van Schilfgaarde and referred to as the "NFP" LMTO code [14]. While in many aspects a development of the earlier described [9] and widely used FP-LMTO formalism, the NFP algorithm incorporates an essential new element, that is, using the "smooth" Hankel functions rather than the "standard" ones for the augmentation of numerical radial solutions in the interstitial region. Whereas the standard spherical Hankel function satisfies the differential equation

$$(\Delta + \epsilon)h_0(r) = -4\pi\delta(\mathbf{r})$$

for $l = 0$, the equation for the smooth function contains the smeared δ function $g_0(r) = C\exp(-r^2/R_{\rm sm}^2)$ as a source term

$$(\Delta + \epsilon)\tilde{h}_0(r) = -4\pi g_0(r)\ ,$$

and the smooth functions of higher orders are generated by applying a differential operator $\mathcal{Y}(-\nabla)$, defined by $\mathcal{Y}(\mathbf{r}) = r^l Y_L$, to the function of the 0th order. These new envelope functions can be tuned by a proper choice of the smoothing parameter $R_{\rm sm}$ to imitate the actual shape of the wavefunction in crystal.

Cubic perovskite ferroelectrics provide an excellent benchmark system for the high-precision total-energy calculation scheme. Whereas one typically cannot pinpoint any essential disagreement in the band dispersions calculated by different full-potential schemes, the energy differences on the $\sim$1 mRy scale related to ferroelectric instability, soft mode phonon frequencies and eigenvectors in these materials may be quite differently estimated by different computation schemes, result in qualitatively different predictions and thus dramatize the competition between different numerical approaches. For $KNbO_3$, a number of calculations has been already done using different methods. Full-potential LAPW calculations were performed by Singh [1–3] and Krakauer *et al* [4,5], LMTO calculations by us [10–13]. In spite of the overall agreement (the ability of both methods to account for the ferroelectric instability, consistent results for the Γ-frozen phonon frequencies), some disagreements prevailed in the description of ferroelectric instability, as well as in the estimation of the soft mode phonon eigenvector [11,3,5].

What makes perovskites generally (and $KNbO_3$ as an example) a hard test for any computational scheme relying on a site-centered basis, like LMTO, is their relatively loose structural packing (if one thinks in terms of nominal ionic radii). The electron density is unevenly distributed between compact NbO_6 octahedra and intermediate large cavities which host small K ions. In our earlier LMTO calculations using the "old" LMTO code by Methfessel [9], good sphere packing was essential for accurate integration over the interstitial region, but could not be guaranteed in a completely satisfactory way (see, e.g. the discussion in Ref. [13]).

TABLE 1. NFP-LMTO calculation setup (κ^2 in Ry, $R_{\mathrm{MT,SM}}$ in a.u.)

K (R_{MT}=1.95)			Nb (R_{MT}=1.85)			O (R_{MT}=1.55)		
n,l	κ^2	R_{SM}	n,l	κ^2	R_{SM}	n,l	κ^2	R_{SM}
$4s$	-0.5	3.0	$5s$	-0.1	2.0	$2s$	-0.5	0.79
$3p$	-0.5	1.3	$4p$	-1.9	0.9	$2p$	-0.15	0.71
$3d$	-0.2	3.4	$4d$	-0.5	1.2	s,p,d	-0.2	2.0
s,p	-0.2	2.0	s,p,d	-1.0	1.5			

In the present implementation of LMTO, the aspect of good sphere packing is no more sensitive, therefore we tried to figure out finally whether the mentioned disagreement with the LAPW results was due to problems of technical inefficiency (unadequate integration scheme etc.) or has to do with some basic limitations of the LMTO formalism.

In our present benchmark calculations, we used the implementation of the full-potential LAPW method knows as the WIEN97 code [15]. Sphere sizes were chosen as shown in the Table 1 (the same for LAPW and LMTO). The **k**-space integration was performed in an identical way in both schemes, using the sampling on a mesh of 18 inequivalent points, corresponding to 6×6×6 divisions of the full Brillouin zone. This mesh was found to be sufficiently dense for the estimations of ferroelectric instability, based on previous experience [2]. The exchange-correlation was treated either in the local density approximation (LDA) or in the generalized gradient approximation (GGA).

In the construction of the LMTO setup, the usual procedure is to optimize the possibly minimal basis, using the freedom in the choice of basis parameters, and then to expand the basis in order to ensure its sufficient completeness. In the NFT formalism, the quality of the basis depends on both energies of the smooth Hankel functions and their smoothing radii, the latter apparently having more pronounced effect. In contrast to earlier FP-LMTO scheme [9] which favored the basis functions with at least three tail energies per orbital for sufficient accuracy, the NFP provides a reasonable description of the valence band states with augmenting just one smooth Hankel function to each; the setup is then refined by adding some other tail functions. The calculation setup we used in the present LMTO calculation is shown in Table 1. It includes 70 basis functions, that can be either somehow more extended, or reduced, to get the desirable compromise between the accuracy and performance. For comparison, the basis size for a LAPW calculation of comparable accuracy should include at least ∼800 augmented plane waves.

The present version of NFP incorporates only the LDA treatment of the exchange/correlation. Another technical drawback is the impossibility to treat the states with different principal quantum number and the same orbital quantum number within the valence band. For $KNbO_3$, we had to include Nb4p states and neglect Nb5p in the valence panel. This seems to be an acceptable compromise, however. More discussion related to the LMTO setup may be found in Ref. [10].

CALCULATION RESULTS AND DISCUSSION

Fig. 1 shows the energy/volume curves as calculated by LAPW in the LDA and in the GGA, and by LMTO in the LDA. First two curves essentially reproduce previous results by Singh [2] aimed at the comparison of LDA and GGA. The energy/volume curve generated now with LMTO (crosses in Fig. 1) practically coincides with that obtained with the LAPW. Absolute energy values lie by ∼0.9 Ry lower with LAPW, understandably due to more complete basis.

For the study of ferroelectric instability, we concentrated on the displacement pattern compatible with the t_{1u} TO phonon modes, i.e. the z-displacements of K(0 0 0), Nb($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) and O_{II} ($\frac{1}{2}\frac{1}{2}0$) with respect to two equivalent O_I ($0\frac{1}{2}\frac{1}{2}$) and ($0\frac{1}{2}\frac{1}{2}$) atoms. In Fig. 2, the energy differences are shown as function of the displacement pattern which roughly corresponds to that in the soft mode, ultimately resulting in the equilibrium structure of tetragonal ferroelectric phase: Nb is displaced twice farther as K relatively to the oxygen cage. We found the calculated energy differences to be extremely sensitive to the quality of the charge density representation in the unit cell. In both methods we used, this expansion is done by the fast Fourier transformation; in WIEN97, the magnitude of the largest reciprocal-space vector G is specified whereas in the NFP-LMTO the number of divisions N along each unit cell edge for a real-space uniform grid has to be explicitly provided. For a perovskite, both cutoffs need to be relatively large in order to achieve a convergency in

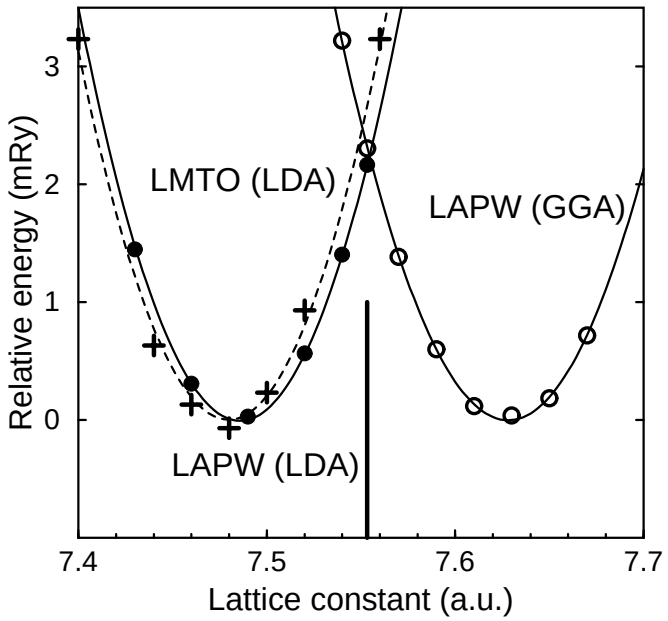

FIGURE 1. Total energy difference (with respect to the equilibrium value) depending on the lattice constant in $KNbO_3$ as calculated by LMTO-LDA (crosses), LAPW-LDA (filled circles) and LAPW-GGA (open circles). The parabolic fit is shown for each case. Experimental lattice constant extrapolated to zero temperature is indicated by a vertical line.

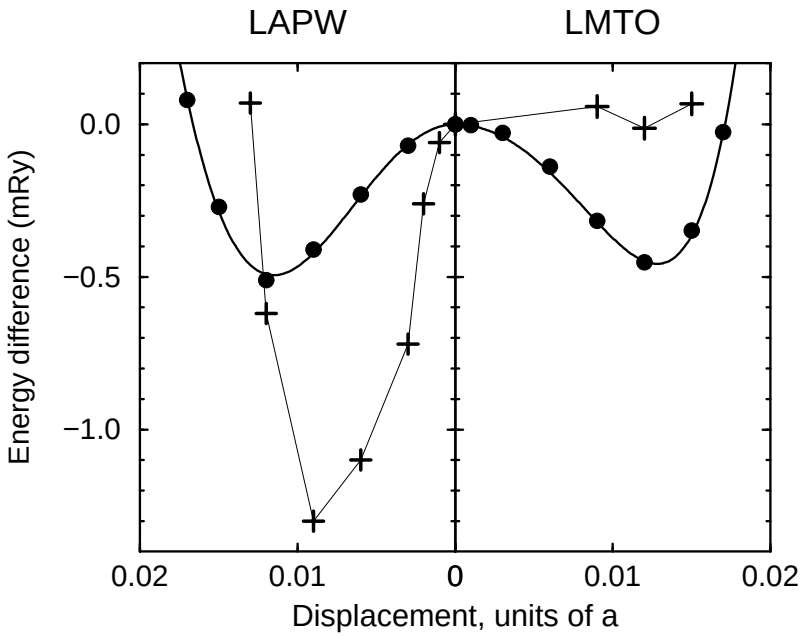

FIGURE 2. Total energy difference depending on atomic displacements $\Delta_z(\mathrm{K}) + 2\Delta_z(\mathrm{Nb})$ as calculated by LAPW and LMTO for different values of Δ_z and different cutoffs in the charge density expansion. Crosses: G=12.0 in LAPW and N=18 in LMTO; dots: G=14.0 in LAPW and N=24 in LMTO (essentially converged results). Polynomial fit is a guide to eye.

TABLE 2. Calculated frequencies and eigenvectors of Γ-TO phonons of the t_{1u} symmetry from LAPW and LMTO

ω	Eigenvectors				ω	Eigenvectors			
(cm^{-1})	K	Nb	$\mathrm{O_I}$	$\mathrm{O_{II}}$	(cm^{-1})	K	Nb	$\mathrm{O_I}$	$\mathrm{O_{II}}$
	LAPW, Ref. [1]					LMTO, Ref. [11]			
$115i$	0.04	−0.60	0.40	0.56	$203i$	0.32	−0.67	0.29	0.53
168	−0.88	0.35	0.19	0.16	193	−0.81	0.12	0.36	0.27
483	0.03	−0.09	0.46	−0.75	459	0.13	−0.14	0.45	−0.75
	LAPW, Ref. [5]					NFP-LMTO, present results			
$197i$	0.01	−0.59	0.42	0.55	$106i$	0.07	−0.61	0.45	0.48
170	−0.88	0.37	0.18	0.15	179	−0.88	0.33	0.21	0.17
473	0.02	−0.08	0.46	−0.76	518	0.03	−0.03	0.41	−0.81

this parameter. As is seen in Fig. 2, the value $G = 10$ in LAPW overestimates the ferroelectric instability whereas the LMTO with $N = 18$ finds yet no trace of the instability. At $G = 12$ and $N = 24$, the trends are about comparable, becoming even closer for $G = 14$ and $N = 32$.

As an additional test for the proper balance of the energetics of different displacement patterns, we calculated the Γ-TO phonons in the cubic phase of $KNbO_3$. The insufficient accuracy of previous LMTO calculations [11,12] manifested itself as a noticeable deviation of the vibration eigenvectors from those obtained by LAPW

[1,5]. Table 2 shows the results of some preliminary calculations with the NFP code (obtained with the 2d-order total energy fit over the results for several combined displacements) in comparison with the LAPW data. One can see that the correct displacement pattern within the soft mode is now restored, and the overall agreement with the LAPW eigenvectors is quite satisfactory.

TREATMENT OF ANHARMONIC VIBRATIONS

With the total-energy fit generally available from first-principles calculations, one may tend to extract some additional information than is possible within the harmonic approximation. The treatment of anharmonic effects in crystal is rather complicated (see, e.g., Ref. [19] for a review). In principle, the modes of different symmetry and related to different **q**-values couple beyond the harmonic approximation. Nevertheless, in the study of ferroelectrics there have been several attempts to single out any particular mode, which is believed to be principally associated with anharmonic effects, and to solve the vibrational Schrödinger equation related to it. This has been done e.g. for $LiTaO_3$ and $LiNbO_3$ by Inbar and Cohen [20] and by Bakker *et al.* [21] (for an empirical potential well, in the latter case) as well as for a one-dimensional A_2 mode in orthorhombic $KNbO_3$ by Postnikov and Borstel [12]. This approach was referred to as non-interacting anharmonic oscillators [20], meaning the oscillators related to a particular Γ TO-mode in crystal. It is assumed that the displacement potential is separable into components with different **q**-dependence. Such separation is less valid for several symmetry coordinates which mix already in the harmonic approximation, therefore the solution of a multidimensional oscillator problem is necessary in this case. A straightforward treatment by, e.g., a finite-difference method on a multidimensional grid rapidly becomes prohibitive with a number of dimensions (see [12]). Therefore, we propose a scheme which uses the expansion in hyperspherical harmonics. This approach is known in the calculation of vibration spectra of three-atomic molecules [22], however, for an *ad hoc* constructed system of variables. In the following, we describe the formalism for an arbitrary number of symmetry coordinates.

We start with an arbitrary convenient set of symmetry-adapted displacement coordinates (see, e.g., Ref. [23]): $S_t = \sum_i B_{ti} x_i$ (x_i are conventional cartesian displacements), which form a complete basis within a particular irreducible representation, but do not need to be orthonormal. The Schrödinger equation then acquires a form:

$$\left[-\frac{\hbar^2}{2} \sum_{tt'} \frac{\partial}{\partial S_t} G_{tt'} \frac{\partial}{\partial S_{t'}} + V(\{S_t\}) \right] \Psi = E\Psi, \tag{1}$$

with the kinetic-energy matrix $G_{tt'} = \sum_i B_{ti} m_i^{-1} B_{t'i}$. Mixed derivatives can further be excluded by the following orthogonalizing transformation:

$$Q_t = \sum_{t'} \frac{X_{t't}}{\sqrt{\lambda^t}} S_{t'},$$

where $X_{t't}$ is the t-th eigenvector, corresponding to the eigenvalue λ^t, of the kinetic-energy matrix. In n-dim. space of generalized coordinates Q_t, we use spherical coordinates $(r, \vartheta_1, \cdots, \vartheta_p, \varphi)$ for $p = n-2$,

$$\begin{aligned} Q_1 &= r\cos\vartheta_1 \\ Q_2 &= r\sin\vartheta_1\cos\vartheta_2 \\ &\cdots \\ Q_{p+1} &= r\sin\vartheta_1\sin\vartheta_2\cdots\sin\vartheta_{p-1}\sin\vartheta_p\cos\varphi \\ Q_{p+2} &= r\sin\vartheta_1\sin\vartheta_2\cdots\sin\vartheta_{p-1}\sin\vartheta_p\sin\varphi \end{aligned}$$

$$0 \le \vartheta_j \le \pi \quad (j = 1, 2, \cdots, p), \quad 0 \le \varphi \le 2\pi\,.$$

There are $(2N+p)(N+p-1)!/(p!\,N!)$ harmonic polynomials of degree N numbered by $n-1$ integers $m_0, \cdots, m_p$ such that $N = m_0 \ge m_1 \ge \cdots \ge |m_p| \ge 0$, $m_p = \pm|m_p|$. The explicit form of the polynomials of is the following:

$$H(N, m_1, .., m_p;\, Q_1, .., Q_{p+2}) = r^N Y^{m_p}_{N,m_1,..,m_{p-1}}(\vartheta_1, .., \vartheta_p, \varphi)\,.$$

The hyperspherical harmonics are chosen either as complex functions

$$Y^{m_p}_{m_0,.,m_{p-1}}(\vartheta_1,.,\vartheta_p,\varphi) = e^{im_p\varphi}\prod_{k=0}^{p-1}(\sin\vartheta_{k+1})^{m_{k+1}} C^{m_{k+1}+\frac{p-k}{2}}_{m_k-m_{k+1}}(\cos\vartheta_{k+1})\,,$$

or in the real form, $\sim \cos m_p$ for $m_p \ge 0$ and $\sim \sin m_p$ for $m_p < 0$. $C^p_n(z)$ are Gegenbauer polynomials [24,25], generated by the following recursion:

$$C^p_0(z) = 1; \qquad C^p_1(z) = 2pz; \qquad (n+1)\,C^p_{n+1}(z) = 2(n+p)\,z\,C^p_n(z) - (n+2p-1)\,C^p_{n-1}(z)\,.$$

$Y^{m_p}_{m_0,.,m_{p-1}}(\vartheta_1,.,\vartheta_p,\varphi)$, orthogonal on a unit sphere, are eigenfunctions of the multi-dimensional Laplace operator:

$$\Delta Y = -\,\frac{m_0(m_0+p)}{r^2}\,Y\,.$$

With the potential and the wave function expanded in hyperspherical harmonics

$$\begin{aligned} V(\vec{Q}) &= \sum_{m_0,..m_p} V_{m_0,..,m_p}(r) Y_{m_0,..,m_p}(\vartheta_1,.., \vartheta_p, \varphi)\,, \\ \Psi(\vec{Q}) &= \sum_{m'_0,..m'_p} R_{m'_0,..,m'_p}(r) Y_{m'_0,..,m'_p}(\vartheta_1,.., \vartheta_p, \varphi)\,, \end{aligned}$$

the multidimensional Schrödinger equation (1) transforms into a system of $\sum_{N=0}^{N_{\max}}(2N+p)(N+p-1)!/(p!\,N!)$ coupled 1-dimensional equations:

$$\begin{aligned} &-\frac{\hbar^2}{2}\,\frac{1}{r^{p+1}}\,\frac{d}{dr}\left[r^{p+1}\frac{dR_{[m]}(r)}{dr}\right] + \frac{m_0(m_0+p)}{r^2}\,R_{[m]}(r) \;+ \\ &+ \sum_{[m'']}\sum_{[m']} V_{[m'']}(r) R_{[m']}(r) \int Y_{[m'']} Y_{[m']} Y_{[m]}\, d\,\Omega = E\,R_{[m]}(r)\,. \end{aligned} \tag{2}$$

The expansion of the potential (provided in a polynomial form by a fit to total-energy values) is finite whereas for the wave function a cutoff value $N_{\max.}$ has to be introduced.

As a practical example of this approach, we considered the solution of a 3-dimensional oscillator problem corresponding to the vibration pattern within the t_{1u} mode in cubic $KNbO_3$. For the symmetry coordinates as discussed above, we included the 4th power of the Nb displacement into the total energy fit. (For real applications, one should of course consider some other degrees of freedom beyond the harmonic approximation). The system of coupled equations (2) was solved by a finite difference method, with 50 points in the equidistant radial mesh from up to $r = 5.0$ where a boundary condition $R(r) = 0$ was imposed on radial wavefunctions (this scheme may be somehow refined in more precise calculations, incorporating a nonuniform mesh). For the maximal degree of polynome $N = 8$ in the wave function expansion, the energy difference between two lowest oscillator levels practically converged to 70 cm^{-1}. The convergence is more slow for higher levels.

CONCLUSIONS

We compare in the present paper the results obtained for the ferroelectric instability in $KNbO_3$ with two methods, LAPW and LMTO, both of which have been applied to this system before but apparently never underwent a thorough comparison with the, as far as possible, identical calculation setup. The result of this comparison is that not only the energy/volume curves are identical in the LDA, but the description of the ferroelectric instability, involving equilibrium displacements of $\sim$0.1 a.u. and energy differences of $\sim$0.5 mRy, is practically identical by both schemes, provided the sufficient accuracy in the description of the charge density variations over the unit cell is guaranteed. The LAPW method provides understandably lower absolute values of the total energy, but the new formulation of LMTO has the advantage of much more compact basis set (about 10 times smaller than that of LAPW) and some resources to expand the basis somehow for even better controllable accuracy without running into numerical problems of overcompleteness. As a useful tool for the analysis of total energy data obtained from any first-principle calculation, we describe the scheme to solve the multi-dimensional vibrational Schrödinger equation in the approximation of non-interacting anharmonic oscillators. The preliminary results for the lowest energy difference are presented for $KNbO_3$.

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